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## Barium accumulation in the Arabian Sea: Controls on barite preservation in marine sediments

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**Abstract**—In this study, a new sequential extraction technique is used to investigate the particulate barium (Ba) phases in sediments from the Arabian Sea to determine the processes controlling Ba accumulation in marine sediments. The total solid-phase Ba concentration in Arabian Sea surface sediments increases with water depth from ~200 ppm at 500 meters below sea surface (mbss) to ~1000 ppm at 3000 mbss. The sedimentary Ba composition consists of three major fractions: barite, Ba incorporated in aluminosilicates, and Ba associated with Mn/Fe oxides. Accumulation of barite, which is the most important Ba fraction in sediments located below 2000 mbss, increases gradually with water depth. The Ba/Al ratio of the terrigenous fraction varies significantly across the Arabian Basin as the result of differences in grain size and provenance of the terrigenous sediment. Ba associated with Mn oxides is a relatively minor fraction compared with bulk Ba concentrations, and it only accumulates in well-oxygenated sediments below the present-day oxygen minimum zone. The water-depth-dependent accumulation of barite in the Arabian Sea is not related to the continuous formation of barite in settling organic particles or Ba scavenging by Mn oxyhydroxides but is primarily controlled by differences in Ba preservation upon deposition. A good correlation between the barite saturation index and the barite accumulation rate in the upper 2000 m of the water column may indicate that the degree of barite saturation of the bottom water is the main environmental factor regulating the burial efficiency of barite. Organic matter degradation, bioturbation, diagenetic Mn cycling, and the crystallinity of the accumulating barite may play additional roles. Copyright © 2001 Elsevier Science Ltd

### 1. INTRODUCTION

Sedimentary barium (Ba) has been recognized as an important proxy for the reconstruction of past variations in oceanic productivity (e.g., Dehairs et al., 1980, 1990; Bishop, 1988; Dymond et al., 1992; Francois et al., 1995). Sediments underlying areas of high primary productivity are often enriched in Ba-bearing solid phases (e.g., Goldberg and Arrhenius, 1958; Brumsack, 1989; Paytan et al., 1996; Nürnberg et al., 1997). Sediment trap data revealed a close relation between the vertical fluxes of organic carbon and particulate Ba (Dymond et al., 1992; Francois et al., 1995; Dymond and Collier, 1996). Barite crystals are common in the suspended matter of the water column (Dehairs et al., 1980), despite the fact that the water column is usually undersaturated (Church and Wolgemuth, 1972; Monnin et al., 1999). The origin of these barite crystals is still poorly understood. Barite is thought to precipitate in microenvironments within decaying organic matter or fecal pellets (Dehairs et al., 1980; Bishop, 1988; Dymond et al., 1992; Francois et al., 1995). This barite formation may be induced by the release of excess sulfate from organic matter degradation (Dehairs et al., 1980; Bishop, 1988) or by dissolution of acantharian-derived celestite (Bernstein et al., 1992). Because interstitial waters are generally saturated with respect to barite, this mineral phase is considered to be less sensitive to diagenesis than organic matter or opal, and hence a better

geochemical proxy for biologic productivity (Dymond et al., 1992; Dymond and Collier, 1996).

Application of sedimentary Ba contents as a proxy for (paleo)productivity is well established for open-ocean settings (e.g., Thompson and Schmitz, 1997; Gingeles et al., 1999), but several problems exist for continental margin areas. First, the relationship between organic carbon and particulate Ba in trap material is poorly constrained for nearshore areas (Francois et al., 1995; Fagel et al., 1999; Dehairs et al., 2000). Lateral transport of refractory organic matter, resuspended barite from continental shelves, or both preclude accurate estimates of export production. Second, early diagenetic processes may significantly affect the preservation of the sedimentary Ba signal (Von Breymann et al., 1992; McManus et al., 1994; 1998). High accumulation rates of reactive organic matter in continental margin areas may induce sulfate reduction, resulting in remobilization of barite (e.g., De Lange et al., 1994; Torres et al., 1996). Third, biogenic barite contents are usually determined from bulk Ba concentrations after correction for the contribution of Ba associated with aluminosilicates coming from the continents (e.g., Dymond, 1981; Francois et al., 1995). This approach, which requires accurate knowledge of the Ba/aluminum (Al) ratio of the aluminosilicate source material, may introduce large errors for sedimentary environments that receive a high supply of terrigenous material (Dymond et al., 1992; Fagel et al., 1999; Gingeles et al., 1999).

In the present study, processes controlling Ba accumulation in surface sediments from the Arabian Sea are investigated. The Arabian Sea is one of the most productive areas in the world. Strong southwestern monsoonal winds cause coastal and open-

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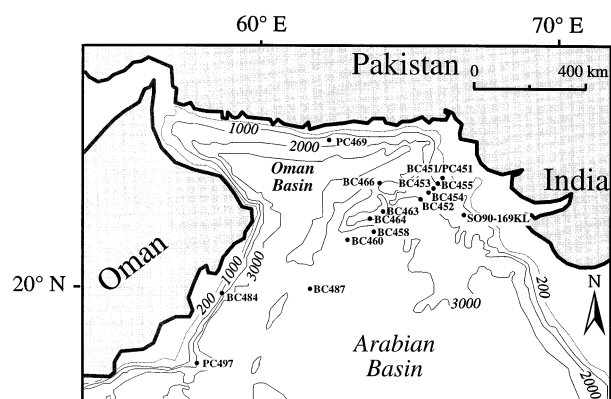


Fig. 1. Sample locations in the northern Arabian Sea of the box and piston cores used in this study.

ocean upwelling off Somalia and Oman during summer (e.g., Wyrtki, 1973; Slater and Kroopnick, 1984). Upwelling nutrient-rich water masses are transported throughout the Arabian Sea, causing a high seasonal productivity (e.g., Qasim, 1982). High downward fluxes of organic matter, in combination with restricted deep-water ventilation, result in an pronounced oxygen minimum zone (OMZ) between 150 and 1250 m of water depth (e.g., Slater and Kroopnick, 1984). The sample sites of this study all lie under highly productive surface waters but differ in water depth, in distance to the continent, and in bottom-water redox conditions. Application of a new sequential extraction technique allows for the direct determination of the barite content of the sediment. We investigate the causes for the increase of Ba accumulation with water depth, previously observed by Von Breyman et al. (1992), and we discuss the implications for the application of Ba as a proxy for (paleo)productivity.

## 2. STUDY AREA AND METHODS

### 2.1. Sample Locations

During the Netherlands Indian Ocean Program in 1992, box core samples were taken in the northern Arabian Sea. For this study, 12 box cores were selected, located on the Pakistan margin (stations 451, 452, 453, 454, and 455), the Oman Margin (station 484), the Murray Ridge (stations 463 and 464), and the Arabian Basin (stations 458, 460, 466,

and 487; Fig. 1, Table 1). Bottom-water oxygen concentrations were derived from oxygen measurements at nearby conductivity temperature depth stations (Table 1). Sedimentation rates were calculated from Accelerator Mass Spectrometry (AMS)  $^{14}\text{C}$ -dated foraminiferal samples from the base of the box cores (Van der Weijden et al., 1999), assuming a constant reservoir age of 400 yr. The average mass accumulation rates (MARs) for each core were calculated as the product of the sedimentation rate and the mean dry bulk density (Table 1).

### 2.2. Pore-Water Analysis and Barite Saturation Calculations

Pore-water extractions were performed on board within 24 h of core collection according to shipboard routine (De Lange, 1992). The box cores were vertically sluiced into a glovebox, which was kept under low-oxygen conditions ( $\text{O}_2 < 0.0005$  volume percentage) and at in situ bottom temperature. Under a nitrogen pressure of up to 7 bar, the pore waters were extracted in Reeburgh-type squeezers. Acidified pore-water samples were taken back to the laboratory and measured for sulfur with a Perkin Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES).

The degree of saturation of the water column with respect to barite in the Arabian Sea was taken as that for GEOSECS station 418 ( $6^\circ 11' \text{N}$ ,  $64^\circ 25' \text{E}$ ) by use of dissolved Ba concentrations, in situ temperatures, and salinities (Ostlund et al., 1987; Monnin et al., 1999). The saturation state was calculated according to the procedure described by Monnin et al. (1999) and Monnin (1999). Undersaturation is indicated by a saturation index (SI) smaller than 1 and supersaturation by a SI greater than 1.

### 2.3. Solid-Phase Analysis

The dry bulk density of the sediment samples was calculated by measuring weight loss of fixed volume samples after freeze-drying. Bulk concentrations of Ba and Al were determined by total dissolution of 250 mg of sample at  $90^\circ\text{C}$  in a 5-mL 6.5:2.5:1 mixture of  $\text{HClO}_4$  (60%),  $\text{HNO}_3$  (65%), and  $\text{H}_2\text{O}$ , and 5 mL HF (40%). After evaporation of the solutions at  $190^\circ\text{C}$  on a sand bath, the dry residue was dissolved in 25 mL 1 mol/L HCl. The resulting solutions were analyzed with the ICP-AES. All results were monitored by use of international (SO1 and SO3) and in-house standards. Relative errors for duplicate measurements were  $< 3\%$ . After removal of all carbonates with 1 mol/L HCl, organic carbon contents ( $\text{C}_{\text{org}}$ ) were measured with a NA 1500 NCS analyzer. Relative errors were  $< 1\%$ .

The distribution of the particulate Ba phases was determined in the surface sediments (0–2 cm) by a sequential extraction technique (Schenau and De Lange, 2000). Approximately 125 mg of dried and powdered sediment was washed sequentially with several different solvents (Table 2). The extracted solutions were measured by ICP-AES. Although this extraction sequence was originally developed for phosphorus, it may also be used to determine the sedimentary Ba

Table 1. Location, water depth, bottom-water oxygen concentration (BWO), bottom-water temperature ( $T_{\text{bottom}}$ ), mass accumulation rate (MAR), and organic carbon ( $\text{C}_{\text{org}}$ ) concentration (in top 2 cm) of the box cores used in this study. Box cores located within the OMZ are boldface.

Sample	Latitude (N)	Longitude (E)	Water depth (m)	BWO ( $\mu\text{M}$ )	$T_{\text{bottom}}$ ( $^\circ\text{C}$ )	MAR ( $\text{g cm}^{-2} \text{ky}^{-1}$ )	$\text{C}_{\text{org top}}$ (wt.%)
<b>BC451</b>	23°41'.4	66°02'.9	495	<2	12.6	12.5	4.1
BC452	22°56'.4	65°28'.1	2001	87.1	3.0	3.8	1.1
BC453	23°14'.0	65°44'.0	1555	39.3	5.0	5.6	1.2
BC454	23°26'.9	65°51'.2	1254	12.5	6.9	6.0	3.4
<b>BC455</b>	23°33'.3	65°57'.2	998	<2	8.7	6.9	4.3
BC458	21°59'.7	63°48'.8	3000	123.7	1.7	4.0	0.8
BC460	21°43'.2	62°55'.2	3262	125.3	1.7	4.5	0.9
<b>BC463</b>	22°33'.6	64°03'.3	970	<2	8.9	5.2	5.7
BC464	22°15'.0	63°34'.7	1511	34.8	5.3	4.3	1.3
BX466	23°36'.1	63°48'.5	1960	75.4	3.1	5.9	0.9
<b>BC484</b>	19°30'.0	58°25'.8	527	<2	12.3	3.8	2.3
BC487	19°54'.8	61°43'.3	3566	151.0	1.6	1.3	0.8

Table 2. Details of the sequential extraction scheme and the extracted Ba fractions.

Step	Extractant	Relative errors (%)	Ba phase extracted
1	8 × 25 mL 2 mol/L NH <sub>4</sub> Cl (brought to pH 7 with ammonia), 4 h, 20°C	<3	Barite (Ba <sub>bar</sub> )
2	1 × 25 mL 0.15 mol/L Na-citrate, 0.5 mol/L NaHCO <sub>3</sub> (pH 7.6), and 1.125 g Na-dithionite, 16 h, 20°C 1 × 25 mL 2 mol/L NH <sub>4</sub> Cl (pH 7), 2 h 1 × 25 mL demineralized water, 2 h	<10	Ba associated with Fe/Mn oxides (Ba <sub>ox</sub> )
3	1 × 25 mL 1 mol/L Na-acetate buffered at pH 4 with acetic acid, 16 h, 20°C 1 × 25 mL 2 mol/L NH <sub>4</sub> Cl (pH 7), 2 h 1 × 25 mL demineralized water, 2 h	—	—
4	25 mL 1 mol/L HCl, 16 h, 20°C 1 × 25 mL demineralized water, 2 h	—	—
5	5 mL of a 6.5:2.5:1 mixture of HClO <sub>4</sub> (60%), HNO <sub>3</sub> (65%), and H <sub>2</sub> O, and 5 mL HF (40%), 16 h, 90°C (total digestion)	<2%	Ba associated with aluminosilicates (Ba <sub>det</sub> )

composition. An extraction with 25 mL of a 2 mol/L NH<sub>4</sub>Cl (pH 7) potentially dissolves ~2000 ppm Ba barite from a 125-mg sediment sample (Rutten, 2001), and accordingly, this extraction can be used to separate barite from Ba associated with aluminosilicates. Carbonates contain very low concentrations of Ba (~30 ppm; Lea and Boyle, 1989), and accordingly, the Ba fraction associated with carbonates, which is also extracted with 2 mol/L NH<sub>4</sub>Cl, can be neglected. The 2 mol/L NH<sub>4</sub>Cl extraction was repeated eight times, but analysis of each individual extraction for some samples indicated that all Ba extractable in this solvent had been extracted in the first two leaches. The Na-dithionite extraction (step 2) has been applied to determine Mn and Fe oxide contents, but also those of elements that are adsorbed on this fraction (e.g., Canfield, 1989). Because barite has been removed in the previous step, aluminosilicates do not dissolve in Na-dithionite (pH 7), and there are no other major particulate Ba phases in marine sediments, it can be assumed that only Ba adsorbed to Mn/Fe oxides is released to solution in step 2. This is confirmed by the results of this study (see below). The detection limit for Ba associated with Mn/Fe oxides (step 2) is 30 ppm (for a 125-mg sample). Here, only the results for steps 1, 2, and 5 are reported because no Ba was extracted in steps 3 and 4. Recovery for Ba with respect to total Ba varied between 96 and 100%. Relative errors of Ba for duplicate measurements for each extraction are given in Table 2. Sedimentary Mn oxide concentrations were determined from the Mn extracted in the Na-dithionite extraction. To study the downcore distribution of Ba in the box cores, total Ba concentrations were determined. Because no sequential extraction results were available for these sediment samples, the excess Ba concentration (Ba<sub>excess</sub>; i.e., Ba not associated with aluminosilicates) was calculated with the following equation:

$$\text{Ba}_{\text{excess}} = \text{Ba}_{\text{tot}} - (\text{Al} \times \text{Ba}_{\text{det}}/\text{Al}) \quad (1)$$

where Ba<sub>tot</sub> and Al are the total Ba and Al concentrations, respectively, and Ba<sub>det</sub>/Al is the Ba/Al ratio of the aluminosilicate fraction, which was determined from the sequential extraction results (step 5) for the top sample of each box core.

To investigate the influence of sediment source vs. grain size on the Ba content of the siliciclastic sediment fraction, the composition of selected size ranges (silt fractions A, B, and C with modal grain sizes of ~5, ~15, and ~40 μm, and sand fraction D with grain sizes of >63 μm) of sediment samples from piston cores were determined. Carbonates, barite, and adsorbed Ba were removed from bulk samples by use of excess 3% HCl. The silt fractions were separated from the bulk siliciclastic fractions by means of a settling tube, and the sand fraction was separated by sieving, which was checked by grain size analysis with a Malvern 2600 laser-diffraction size analyzer. Subsequently, the grain size fractions were totally dissolved and analyzed by use of the same procedure as for bulk sediment samples.

### 3. RESULTS AND DISCUSSION

#### 3.1. Ba Accumulation in Arabian Sea Surface Sediments

The total Ba concentration in surface sediments increased almost linearly ( $r^2 = 0.97$ ) with water depth (Fig. 2). The sedimentary Ba/Al ratio (Ba<sub>tot</sub>/Al<sub>tot</sub>) increased from ~4.4 mg/g at 550 meters below sea surface (mbss) to ~27.5 mg/g for the deepest pelagic sites (Table 3). These results agree well with previous studies from the Oman Margin (Hermelin and Shimmiel, 1990; McManus et al. 1998; Fig. 2), indicating that this increase in solid-phase Ba concentration with water depth occurs over the whole northern part of the Arabian Basin.

The Ba distribution among solid phases in surface sediments showed large fluctuations (Table 3; Fig. 3). Ba incorporated in barite (Ba<sub>bar</sub>) became a relatively more important fraction relative to Ba associated with aluminosilicates (Ba<sub>det</sub>) with increasing water depth. The sequential extraction scheme used for this study cannot distinguish barite from a biogenic origin or from a hydrothermal origin. Accumulation of hydrothermal barite is restricted to areas of hydrothermal activity (Dymond et al., 1992). In the absence of important hydrothermal vents, the contribution of hydrothermal barite is probably negligible in the northern Arabian Sea. The Ba<sub>det</sub> concentrations were higher near the Pakistan Margin (200–260 ppm) compared with more offshore pelagic stations (100–150 ppm). Accordingly, the two box cores from Murray Ridge (BC463 and BC464) had a relative lower contribution of Ba<sub>det</sub> compared with the Pakistan continental slope from a similar water depth. Ba associated with Fe-Mn oxides (Ba<sub>ox</sub>) was a relatively small fraction compared with the other Ba species and only became detectable in sediments located below a water depth of 1500 m.

The Ba<sub>det</sub>/Al ratios of the surface sediments (Fig. 2) were significantly lower than those reported for average shales (6.25 mg/g; Bowen, 1979). This may be explained by the fact that most natural shales contain small amounts of other Ba phases, such as barite. The Ba<sub>det</sub>/Al ratios decrease with water depth, which may reflect either a change in grain size, a change in provenance of the sediment, or a combination of the two. To assess the influence of these two parameters, we analyzed the composition of four grain size ranges in sediment samples from

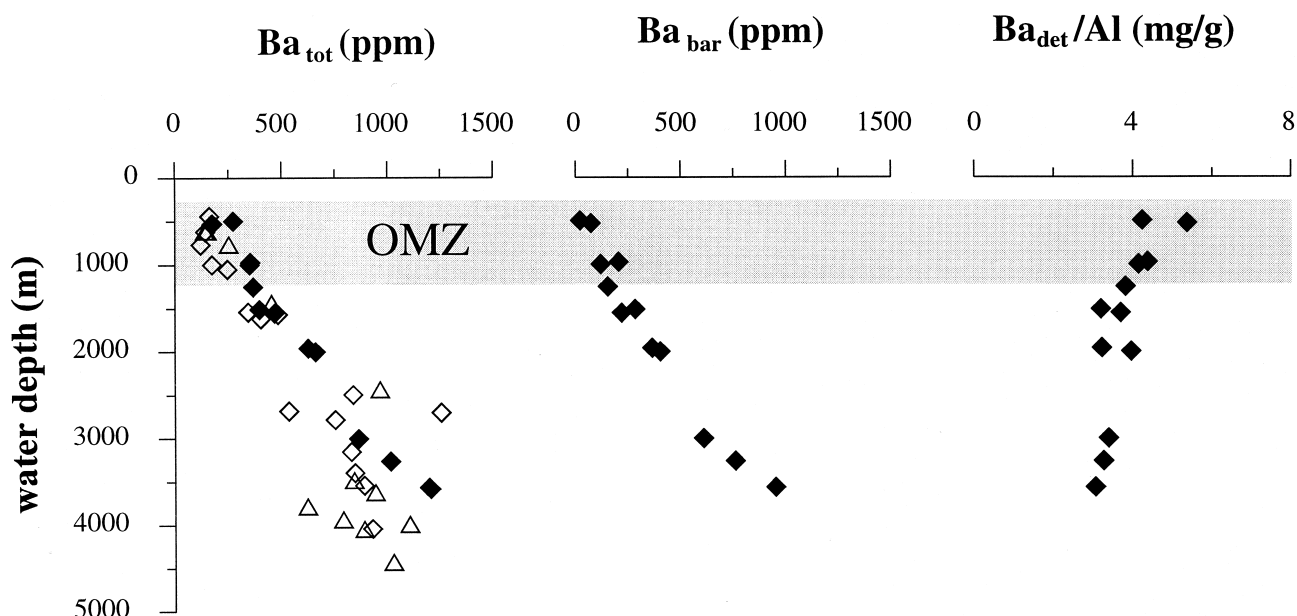


Fig. 2. A plot of bulk Ba concentrations ( $Ba_{tot}$ ), Ba barite concentrations ( $Ba_{bar}$ ), and bulk Ba/Al ratios ( $Ba_{det}/Al$ ) of surface sediment samples (0–2 cm) vs. water depth (◆). In the plot of the bulk Ba concentrations, data from previous studies are also shown (Hermelin and Shimmield, 1990 (Δ); McManus et al., 1998 (◇)). The shaded area indicates the position of the OMZ ( $<2 \mu M O_2$ ).

four piston cores. Terrigenous sedimentation at sites PC451 and SO90 to 169KL (Pakistan slope) is dominated by the input from the Indus River drainage area, at site PC469 (Makran Margin) by the input from the Makran, northern Arabian Peninsula and Persian Gulf area, and at site PC497 (Oman Margin) by the input from the central Arabian Peninsula (Prins and Weltje, 1999). In these four pistons, a marked increase of the  $Ba_{det}/Al$  ratio with grain size was observed in all studied sediment samples (Fig. 4). This trend was most evident in the Oman Margin sediments, less in the Pakistan slope sediments, and minor (to nonexistent in the silt fraction) in the Makran Margin sediments. Besides this grain-size effect, a clear compositional trend was observed for the three different source areas. Sediment fractions from the Arabian or Makran sources had a distinctly different  $Ba_{det}/Al$  ratio than the Indus source

(Fig. 4). The water-depth-dependent decrease of the  $Ba_{det}/Al$  ratio (Fig. 2) may be explained by the combination of variations in grain size and source area of the deposited material. A basinward-fining trend has been observed in the late Quaternary sediment records from the Pakistan continental slope (Prins and Weltje, 1999). The decrease in the  $Ba_{det}/Al$  ratio with water depth may thus be related to the relative increase of fine-grained sediments at the deeper, more offshore sites. Furthermore, the deepest box cores from the data set presented here (BC458, BC466, and BC487) had a more western position and therefore received more eolian material from the Arabian source compared with the more shallow box cores from the Pakistan slope (BC451, BC455, BC452, BC453, and BC454; Prins and Weltje, 1999). The spatial and temporal variations in the composition of the siliciclastic sediment fraction illustrate

Table 3. Bulk Ba concentrations ( $Ba_{tot}$ ), bulk Ba aluminum ratios ( $Ba_{tot}/Al$ ), Ba speciation, barite accumulation rates ( $Ba_{bar}AR$ ), and organic carbon barite ratios ( $C_{org}/Ba_{bar}$ ) of the surface sediment samples used in this study.

Sample	$Ba_{tot}$ (ppm)	$Ba_{tot}/Al$ (mg/g)	$Ba_{bar}$ (ppm)	$Ba_{ox}$ (ppm)	$Ba_{det}$ (ppm)	$Ba_{bar}AR$ ( $\mu g cm^{-2} y^{-1}$ )	$C_{org}/Ba_{bar}$ (g/g)
BC451	274	4.44	21	BDA	261	0.262	1947
BC452	660	12.54	403	45	208	1.526	27
BC453	467	8.12	219	24	212	1.226	56
BC454	366	6.74	152	BDA	207	0.925	220
BC455	341	6.3	119	BDA	215	0.823	359
BC458	863	17.05	608	81	171	2.433	12
BC460	1014	20	759	83	165	3.385	11
BC463	353	10.86	205	BDA	142	1.059	277
BC464	396	11.91	283	BDA	106	1.207	44
BC466	626	9.79	364	33	205	2.16	24
BC484	175	8.78	73	BDA	107	0.276	315
BC487	1197	27.53	951	126	130	1.82	8

Below detectable limit.



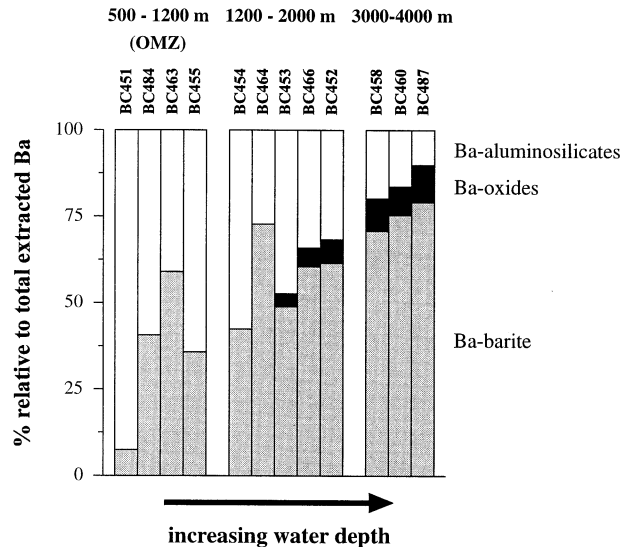


Fig. 3. The solid-phase Ba speciation relative to total extracted Ba for the surface sediment samples (0–2 cm) of this study.

the problem of using a constant  $Ba_{det}/Al$  ratio to calculate the barite content from bulk Ba concentrations.

Excluding the coastal upwelling area offshore Oman, primary productivity rates are at present rather similar throughout the northern Arabian Sea (Qasim, 1982; Banse, 1987; Lee et al., 1998; Van der Weijden et al., 1999). Surface water productivity is somewhat higher for the Pakistan coastal area

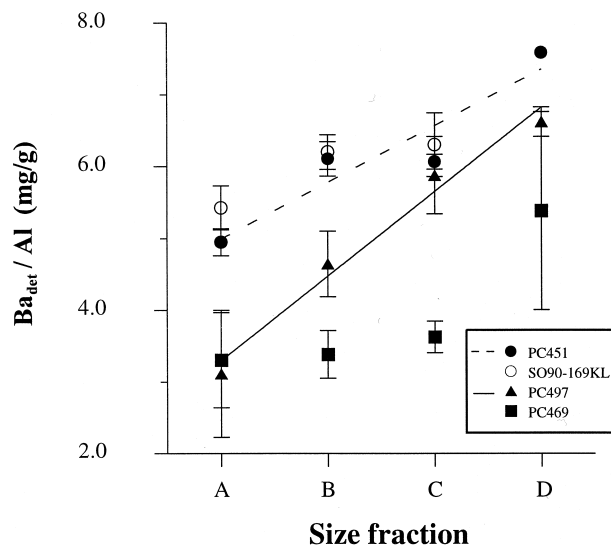


Fig. 4. Plot of the  $Ba_{det}/Al$  ratio (mg/g) vs. selected grain size ranges (silt fractions A, B, and C, with modal grain sizes of  $\sim 5$ ,  $\sim 15$ , and  $\sim 40$   $\mu m$ , and sand fraction D, with grain size of  $> 63$   $\mu m$ ) of sediment samples. The terrigenous sediments from piston cores PC451 and SO90 to 169KL (Pakistan slope) are dominantly supplied from the Indus River drainage area (eolian and fluvial sediments), whereas sedimentation at site PC469 (Makran Margin) is dominated by the input of fluvial and eolian sediments from the Makran Margin and eolian dust from the northern Arabian Peninsula and Persian Gulf area. Sedimentation at site PC497 (Oman Margin) is dominated by the input of eolian dust from the central Arabian Peninsula.

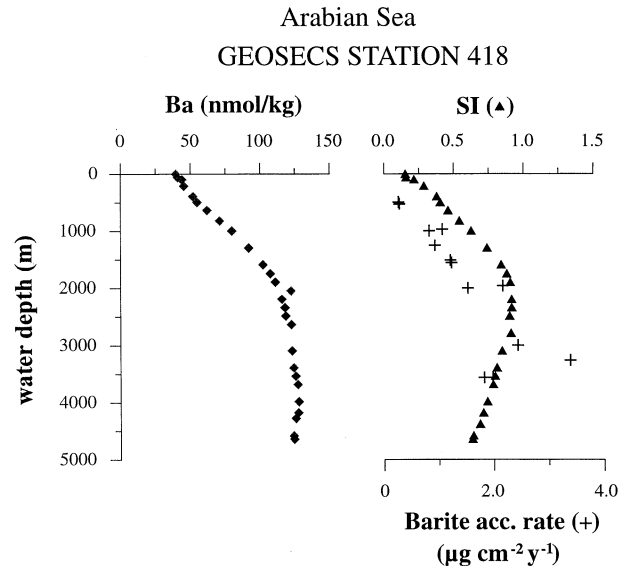


Fig. 5. Dissolved Ba concentrations ( $nmol\ kg^{-1}$ ; Ostlund et al., 1987) and the calculated barite SI for GEOSECS station 418. Also shown is the barite accumulation rate ( $\mu g\ cm^{-2}\ yr^{-1}$ ) for the sample stations of this study.

compared with the open-ocean region, but this difference is less than a factor of two (Qasim, 1982; Pollehne et al., 1993; Brock et al., 1994). The barite distribution in the surface sediments, therefore, does not directly reflect the pattern of present-day productivity in the northern Arabian Sea. A depth dependency of Ba accumulation in areas of high surface water productivity has also been observed for the continental margins off Peru (Von Breyman et al., 1992), Namibia (Calvert and Price, 1983), and California (McManus et al., 1999). The increase of sedimentary barite concentrations with water depth has been attributed to an amplification of the particulate Ba rain rate during transport through the water column as the result of ongoing barite formation in microenvironments and higher Ba preservation in deep pelagic environments attributable to less diagenetic barite regeneration (Von Breyman et al., 1992). In the next sections, we will discuss particulate Ba production in the water column and sedimentary barite preservation to determine what processes control Ba accumulation in marine sediments.

### 3.2. Particulate Ba Production in the Water Column

Sediment trap studies have demonstrated that the vertical flux of particulate Ba sharply increases with depth in the upper part of the water column, indicating that biogenic barite mainly precipitates between 200 and 600 m water depth (Dymond et al., 1992; Dymond and Collier, 1996; Dehairs et al., 2000). This is explained by the fact that labile organic sulfur compounds, acantharian-derived celestite, or both are preferentially regenerated or dissolved within the upper few hundred meters of the water column (Dehairs et al., 1980; Matrai and Eppley, 1989). Ba removal in the upper part of the oceans is consistent with the nutrient-like distribution of Ba in the water column (e.g., Fig. 5; Dehairs et al., 1980; Monnin et al., 1999), radium isotopes in sediment trap material (Moore and Dymond, 1991;

Legeleux and Reys, 1996), and the presence of barite crystals in surface waters (Bishop, 1988; Dehairs et al., 1990). In the deeper part of the water column, the Ba rain rate slightly increases with depth as the result of ongoing organic matter degradation or lateral advection of particulate Ba, but this increase is relatively small compared with the total Ba flux (Dymond et al., 1992; Dymond and Collier, 1996). This pattern of barite formation in the water column, which seems to be characteristic of all major ocean basins, does not correspond to the gradual increase in Ba accumulation rate with water depth in the Arabian Sea.

Potentially, the oxygen-depleted waters at midwater depth could have affected barite formation in the Arabian Sea. It has been suggested that barite precipitation in microenvironments requires a delicate balance in redox conditions to trap sulfate in excess of the seawater concentrations (Dymond and Collier, 1996). In an oxygen-depleted water column, sulfate reduction in anoxic microenvironments may result in the release of sulfides, thereby inhibiting barite formation. However, no evidence so far has been found that the Ba rain rate is significantly lower in areas characterized by an intense oxygen minimum zone. In fact, a maximum of suspended Ba particles at mesopelagic depth often coincides with the oxygen minimum zone as the result of the release of barite microcrystals from decomposing biogenic aggregates (Dehairs et al., 1990). In addition, barite accumulation would be significantly reduced in sediments below the oxygen minimum zone as the settling organic debris would have lost most of its labile organic sulfur at midwater depth, which is not the case for Arabian Sea sediments (Table 3; Fig. 2). Consequently, there is no reason to assume that the low barite accumulation rates for sediments deposited between 500 and 1200 mbss are caused by the lack of barite formation in the water column, but is rather related to a lower preservation of barite upon deposition.

Barite formation in the water column may also be dependent on the source of the settling organic matter. The  $C_{org}/Ba_{bar}$  ratios of suspended matter are usually higher for areas near continental margins (e.g., Fagel et al., 1999), which has been related to the input of refractory organic matter from the shelves and continents (Francois et al., 1995). As this advected material has lost most of its labile sulfur, further barite formation in the water column is precluded. This process may be reflected in the  $C_{org}/Ba_{bar}$  ratios in the surface samples of OMZ sediments (500–1200 m), having significantly higher  $C_{org}/Ba_{bar}$  ratios compared with deeper sites (Fig. 6). By use of results from two sediment traps employed in the southern part of the Arabian Sea ( $C_{org}/Ba_{bar} = 109$  and 155 for 2787 and 3024 mbss, respectively), Francois et al. (1995) calculated that ~72% of the organic carbon flux from this location may be derived from refractory organic debris. A similar high contribution of refractory organic matter seems unlikely for the northern Arabian Sea, where primary productivity is much higher. A study on the nature of the organic matter deposited in the box cores of this study indicated that the organic matter is primarily of an autochthonous origin (Van der Weijden et al., 1999). Furthermore,  $C_{org}/Ba_{bar}$  ratios in samples of the more offshore Murray Ridge do not differ from the near shore samples of the Pakistan Margin (Table 3). Therefore, the  $C_{org}/Ba_{bar}$  ratios for OMZ surface sediments, which are significantly higher than those measured in suspended matter (Dymond et

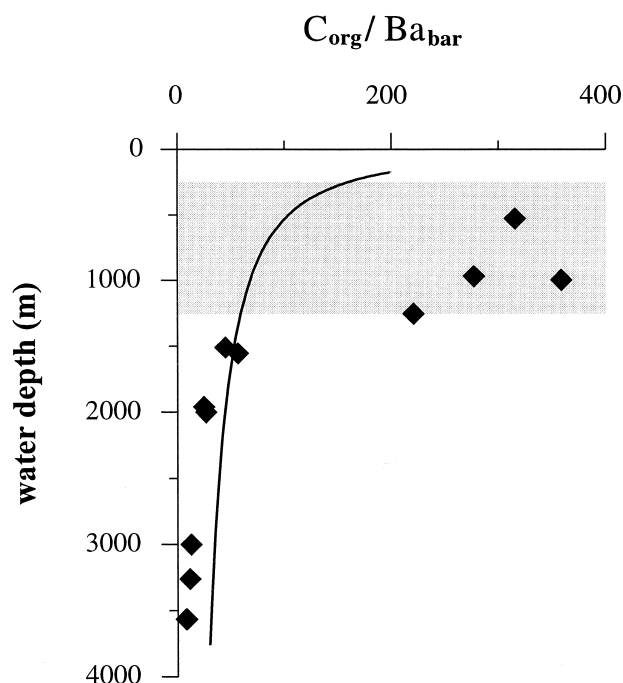


Fig. 6. Plot of the  $C_{org}/Ba_{bar}$  ratios in surface sediments vs. water depth. The solid line represents the  $C_{org}/Ba_{bar}$  ratio of suspended material for open-ocean environments (Francois et al., 1995). The shaded area indicates the position of the OMZ ( $<2 \mu M O_2$ ).

al., 1992; Francois et al., 1995; Fig. 6), reflect a lower preservation factor of barite relative to organic carbon rather than a difference in source material.

The  $C_{org}/Ba_{bar}$  flux ratios of suspended matter have been used to relate the flux of particulate Ba through the water column to the export production (Dymond et al., 1992; Francois et al., 1995; Dehairs et al., 2000). When the export production is known, these empirical equations can be used to estimate the barite deposition flux. Here we have used the rewritten transfer functions for respectively open ocean (Francois et al., 1995; Dehairs et al., 2000):

$$F_{babar} = 0.430 \times Exp^{0.665} \times z^{0.0625} \quad (2)$$

and for continental margin systems (Dehairs et al., 2000):

$$F_{babar} = 0.124 \times Exp^{0.665} \times z^{0.0924} \quad (3)$$

where  $F_{babar}$  is the flux of particulate Ba ( $\mu g cm^{-2} yr^{-1}$ ),  $Exp$  the export production ( $g C m^{-2} yr^{-1}$ ), and  $z$  the water depth (m). The annual export production for the northern Arabian Sea is not well constrained because of its high seasonality. Sediment trap studies have recorded organic carbon fluxes (100 mbss) varying from  $<10$  to  $>300 mg C m^{-2} d^{-1}$  (Pollehne et al., 1993; Buesseler et al., 1998; Lee et al., 1998). Here we have used an annual export productivity of  $40 g C m^{-2} yr^{-1}$  for all stations. This choice is somewhat arbitrary, but the important assumption for this study is that the annual export production is more or less constant for the northern Arabian Sea (Qasim, 1982; Banse, 1987; Lee et al., 1998; Van der Weijden et al., 1999). Subsequently, the calculated barite fluxes for both open margin systems and continental margin systems have been used

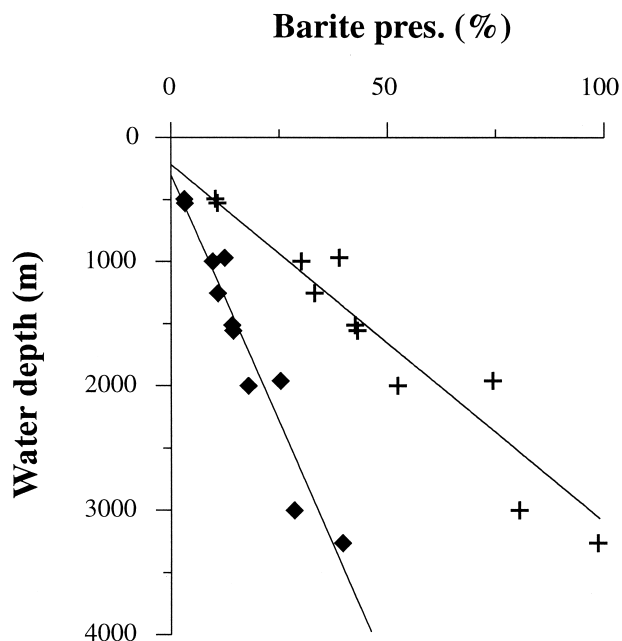


Fig. 7. Preservation of barite (%) calculated from the barite accumulation rates in surface sediments (Table 3) and the estimated Ba deposition fluxes (Eqns. 1 and 2) for respectively an open-ocean ( $\diamond$ ) and a continental margin environment (+) (see text).

to estimate preservation of barite [ $Ba_{\text{bar}}$  pres. (%)] in the surface sediments in the Arabian Sea by use of the equation

$$Ba_{\text{bar}} \text{ pres. (\%)} = 100 \times (B/F_{\text{Babar}}) \quad (4)$$

where  $Ba_{\text{bar}}AR$  is the accumulation rate of barite ( $\mu\text{g cm}^{-2} \text{ yr}^{-1}$ ; Table 3). Both expressions indicate an almost linear increase in barite preservation with water depth (Fig. 7). In absence of detailed published sediment trap data for the northern Arabian Sea, it is not possible to determine the absolute preservation factors of barite. However, on the basis of what is known of barite formation in the water column, we can conclude that barite preservation in the Arabian Sea is very low (0–10%) in sediments from 500 m water depth and increases with water depth. Apparently, it is unlikely that continuous growth of barite crystals during transit through the water column alone can account for the increase in Ba accumulation with water depth in the Arabian Sea.

Another potential source of Ba accumulation in the oceans is Ba scavenged from seawater by Mn and Fe oxides (e.g., Kenison Falkner et al., 1993; De Lange et al., 1994). In the Arabian Sea, dissolved Mn is removed at the base of the OMZ by oxidative scavenging (Schenau, 1999). Deposition of Mn oxides only occurs in sediments located below the OMZ (Fig. 8), where bottom-water oxygen concentrations are sufficiently high to prevent reduction in the water column, at the sediment–water interface, or both. Accordingly, deep oxygenated sediments receive an additional input of Ba adsorbed to Mn oxides compared with the more shallow sediments located within the OMZ, which is reflected by the Ba composition (Fig. 3). The Mn oxide concentration in surface sediments located below the OMZ correlates with the  $Ba_{\text{ox}}$  fraction ( $r^2 = 0.69$ ;  $n = 6$ ), corresponding with an average Ba concentration in Mn oxides

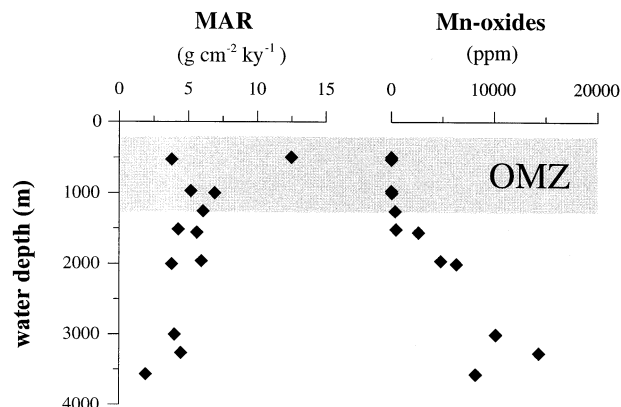


Fig. 8. A plot of the mass accumulation rate (MAR;  $\text{g cm}^{-2} \text{ ky}^{-1}$ ) and the concentration of Mn associated with oxides in the upper centimeter of the sediment (ppm) vs. water depth. The shaded area indicates the position of the OMZ ( $<2 \mu\text{M O}_2$ ).

of  $\sim 6000$  ppm ( $\text{MnO}_2$ ). These values are higher than previously reported (2000 ppm; Dymond et al., 1981). It is possible that some of the  $Ba_{\text{ox}}$  fraction is associated with iron oxides, although no positive correlation with the iron oxide content was observed. In addition, some of the  $Ba_{\text{ox}}$  may have coprecipitated within newly formed Mn oxides during early diagenesis and might thus not originate from scavenging in the water column. Analysis of sediment trap material recovered from the Pacific and Atlantic Oceans indicated that only a minor fraction of the total Ba rain rate is associated with Ba adsorbed to oxyhydroxides (Dymond et al., 1992; Kumar et al., 1996). Kenison Falkner et al. (1993) showed that the distribution of dissolved Ba in a partially anoxic water column is not significantly affected by Fe and Mn redox cycling. This is consistent with the sequential extraction results of this study, which indicate that the  $Ba_{\text{ox}}$  fraction is always much smaller than the other Ba fractions. Although Ba scavenging by oxides in the water column does contribute to higher Ba deposition rates in deepest part of the Arabian Basin, this process does not significantly influence the total Ba accumulation rates.

In short, the water-depth-dependent accumulation of barite in the Arabian Sea is not related to continuous formation of barite in settling organic particles or Ba scavenging by Mn oxyhydroxides, but is primarily controlled by differences in Ba preservation after deposition.

### 3.3. Factors Governing Barite Preservation

The processes governing the preservation of barite in marine sediments are still poorly understood. In general, Ba pore-water profiles are characterized by a sharp increase in concentration in the upper centimeter (e.g., Paytan and Kastner, 1996; McManus et al., 1998). The steep pore-water gradient sustains a diffusive flux of  $Ba^{2+}$  to the bottom water, indicating that a significant fraction of solid-phase Ba is recycled upon deposition. Dissolved Ba concentrations usually reach a more or less constant value just below the sediment–water interface, indicating that the pore water has reached saturation with respect to solid-phase Ba phase (Church and Wolgemuth, 1972; Paytan and Kastner, 1996). These pore-water characteristics, which



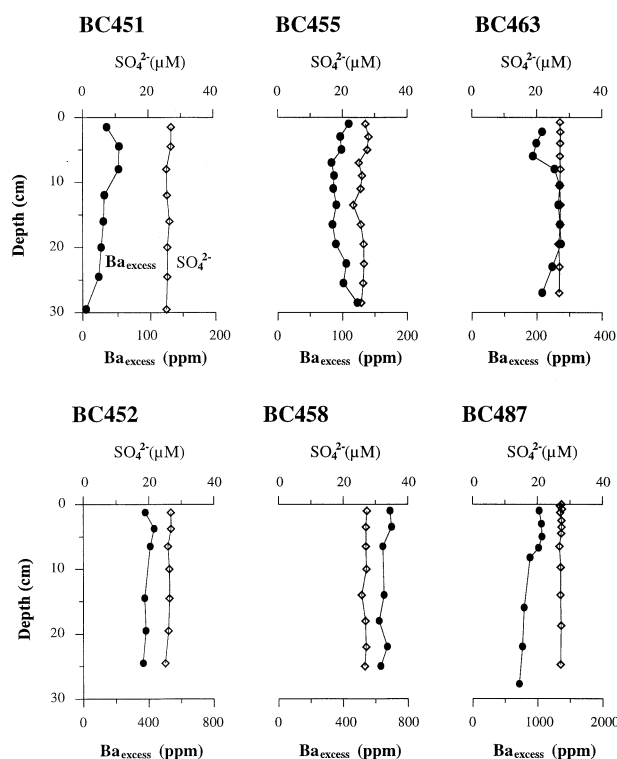


Fig. 9. Depth profiles for pore-water sulfate ( $\diamond$ ) and excess solid-phase Ba concentration ( $\blacklozenge$ ) ( $\text{Ba}_{\text{excess}}$ ; i.e., Ba not associated with aluminosilicates) for six box cores. The profiles for the box cores not shown in this figure all display the same pattern with sediment depth.

have been recorded for both oxic and suboxic environments as well as for continental margin and deep pelagic settings (Church and Wolgemuth, 1972; Paytan and Kastner, 1996; McManus et al., 1998), indicate that barite remobilization in marine sediments occurs primarily briefly after deposition. Unfortunately, no Ba pore-water profiles are available for the box cores of this study. However, the solid-phase  $\text{Ba}_{\text{excess}}$  concentrations, which show no major change with depth in all box cores (Fig. 9), indicate that also for the Arabian Sea, barite regeneration is primarily restricted to the upper centimeter of the sediment. Next we will discuss three environmental conditions that may affect this early diagenetic barite dissolution: the mass accumulation rate, the redox conditions of bottom water and sediment, and the Ba concentration of the overlying bottom water.

### 3.3.1. Mass Accumulation Rate

Dymond et al. (1992) proposed that Ba regeneration is mainly controlled by the sediment accumulation rate: rapid burial will shorten the period during which the sediment is exposed to undersaturated bottom waters, thereby increasing preservation of barite. These authors presented the following tentative relationship between Ba preservation and MAR ( $\mu\text{g cm}^{-2} \text{ yr}^{-1}$ ):

$$\text{Ba pres. (\%)} = 20.9 \log (\text{MAR}) - 21.3 \quad (5)$$

This equation, when applied to the Arabian Sea surface sedi-

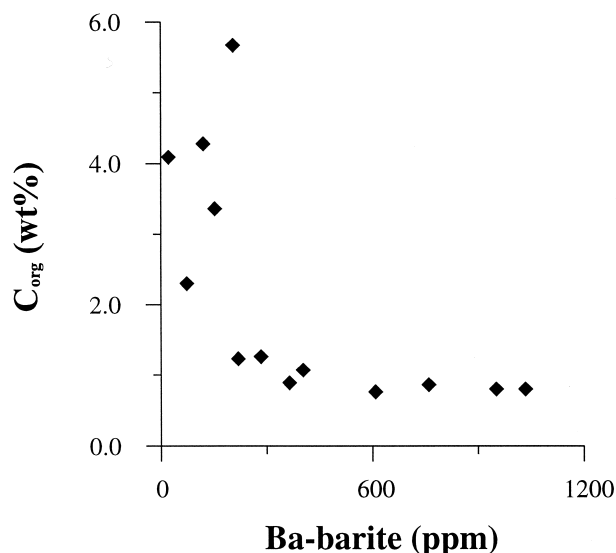


Fig. 10. Plot of the Ba-barite (ppm) vs. organic carbon concentration (wt.%) of surface sediments.

ments, leads to preservation factors varying between 47% (BC487) and 64.3% (BC451). These high preservation factors cannot account for the low barite accumulation rates observed for continental margin sites. Furthermore, mass accumulation rates for our data set do not vary significantly with water depth (Fig. 8), and therefore cannot explain the changes in preservation. Obviously, the mass accumulation rate is not the master variable controlling barite preservation in the Arabian Sea. A similar conclusion was reached for sediments from the northern Atlantic Ocean (Kumar et al., 1996) and the California Margin (McManus et al., 1999).

### 3.3.2. Redox Conditions

Low Ba contents in organic-matter-rich sediments on the continental margin have been attributed to barite remobilization in sulfate-depleted pore waters (Brumsack, 1989; Von Breyermann et al., 1992; Torres et al., 1996). In our study, pore-water sulfate profiles show no decrease with sediment depth (Fig. 9), indicating that organic matter degradation in the top sediments is not governed by sulfate reduction. Sulfate reduction, however, may also occur within anoxic microenvironments in suboxic or oxic sediments (Berelson et al., 1996). Although the reduced sulfur produced is normally rapidly reoxidized, it has been argued that these localized sulfate depletions may reduce Ba preservation under certain suboxic conditions (McManus et al., 1994, 1998). Accordingly, sediments located within the OMZ may be subject to enhanced barite regeneration. It may be argued, however, that most barite crystals are released from biogenic aggregates at intermediate water depth as free particles (e.g., Dehairs et al., 1990) and that the deposited barite will therefore no longer be directly incorporated in the organic debris. Furthermore, there is no apparent negative correlation between the sedimentary organic carbon and barite concentrations (Fig. 10). Sediments with rather constant organic carbon contents of 1 wt.% show large variations in Ba-barite concentrations. The potential influence of barite dissolution in sulfate-

depleted microenvironments is probably limited, although on the basis of the present results, it is not possible to entirely rule out a possible effect of early diagenetic organic matter remineralization on barite preservation.

Ba burial may also be affected by early diagenetic Mn cycling (Schroeder et al., 1997; McManus et al., 1998). Presently, Mn and Fe oxides are reduced in the northern Arabian Sea near the sediment–water interface for OMZ sediments and at a sediment depth between 2 and 10 cm for oxygenated sediments located at 2000 to 3500 mbss (Passier et al., 1997; Van der Weijden et al., 1999). Thus, the  $Ba_{ox}$  fraction is not a permanent sink for Ba. However,  $Ba^{2+}$  released to the pore water by barite dissolution may be scavenged by Mn oxyhydroxides in the oxic zone of the sediment. The subsurface enrichment of Mn oxides present in the deep Arabian Basin (>2000 mbss) may act as a near-surface trap for Ba, similar to what has been observed in the diagenetic cycling of phosphate (e.g., Sundby et al., 1992). The potential effect of Ba cycling with Mn oxides has not yet been investigated. Sediment profiles of  $Ba_{excess}$ , which show no simultaneous decrease with Mn at these sediment depths, provide no evidence for active Ba cycling in the subsurface (Fig. 9). The relative importance of diagenetic Mn scavenging is therefore probably limited, as barite dissolution occurs mainly near the sediment–water interface and most of the released  $Ba^{2+}$  is directly lost to the bottom water.

Thus far, bioturbation has not received much attention in the diagenetic cycling of Ba. It may be argued that intensive mixing by benthic organisms will introduce barite more rapidly into the deeper saturated part of the sediment. In this way, preservation of marine barite would be favored in more oxygenated environments below the OMZ. In the Arabian Sea, the mean mixed-layer depth for OMZ sediments is lower than well-oxygenated Atlantic and Pacific sediments from similar water depths (Smith et al., 2000). However, some bioturbation does occur in the box cores taken between 500 and 1200 m, as is indicated by the presence of benthic foraminifers and the absence of laminae. Moreover, it was found that the mixed-layer depth and bioturbation intensity were not significantly different in a transect through the OMZ offshore of Oman (Smith et al., 2000). Clearly, more information is needed to evaluate the influence of bioturbation on barite preservation.

### 3.3.3. Bottom-Water Barite Saturation

It has been suggested that the Ba concentration of the bottom water may affect preservation of sedimentary Ba (Francois et al., 1995; Jeandel et al., 1996). As barite regeneration predominantly takes place shortly after deposition, the degree of undersaturation of the bottom water with respect to barite may have a high impact on its dissolution rate. Recently, Monnin et al. (1999) have calculated the degree of barite saturation for all major oceanic reservoirs. In the Arabian Sea (GEOSECS station 418), the SI gradually increases with water depth and approaches saturation at 2000 mbss, with a maximum SI of ~0.91 (Fig. 5). Below 2500 mbss, the degree of saturation decreases again. The gradual increase in the SI with water depth in the upper 2000 m of the water column corresponds to a similar increase in barite accumulation (Fig. 5). This points to a direct relation between the degree of barite saturation of the

bottom water and Ba preservation in the sediment. The reduction in the SI below 2500 m is not clearly reflected by a similar decrease in the Ba accumulation rate for sediments deposited between 3000 and 3600 m, but this is possibly due to the limited amount of data for the deeper part of the water column.

Because no pore-water Ba profiles are available for the data set presented here, it is not possible to determine the benthic regeneration rate of Ba. The potential influence of the SI on barite preservation in the Arabian Sea, however, may be demonstrated with the following calculations. The diffusive Ba flux from the sediment ( $J_{Ba}$ ;  $nmol\ cm^{-2}\ yr^{-1}$ ) can be estimated with Fick's first law (Berner, 1980):

$$J_{Ba} = \phi D_s (C_0 - C_{bottom})/z \quad (6)$$

where  $\phi$  is the porosity in the upper centimeter,  $D_s$  the whole sediment diffusion coefficient for Ba,  $C_0$  the “equilibrium” Ba concentration of the pore water that is reached just below the sediment water interface,  $C_{bottom}$  the Ba bottom-water concentration, and  $z$  the sediment depth where the equilibrium Ba concentration is reached. The whole sediment diffusion coefficient is expressed by the following equation (Boudreau, 1997):

$$D_s = D^*/1 - \ln(\phi^2) \quad (7)$$

where  $D^*$  is the diffusion coefficient of Ba in seawater ( $4.04 \times 10^{-6}\ cm^2\ s^{-1}$  at  $0^\circ C$ ), corrected with the Stokes-Einstein relation for the in situ bottom-water temperature (Li and Gregory, 1974), and  $\phi$  the sediment porosity (here, the average porosity of 0.8 is used). In this theoretical situation (i.e., ignoring the influence of variations in sedimentation rate, sediment porosity, bioturbation, and redox conditions), we assume that  $z$  is constant for all water depths. The sediment depth  $z$  where the equilibrium Ba concentration is reached has been found to vary between 1 and 10 mm (Paytan and Kastner, 1996; McManus et al., 1998). Dissolution of barite is a surface-controlled reaction (Berner, 1980; Dove and Czank, 1995), and the saturation depth  $z$  is therefore primarily dependent on the barite deposition flux. Accordingly, higher deposition rates of barite will result in higher Ba benthic fluxes, which has indeed been observed for the Equatorial Pacific region (Paytan and Kastner, 1996). As discussed, the Ba rain rate in the deeper part of the water column does not change much with water depth, and therefore, the depth of saturation can be expected to be constant. Furthermore, we assume that  $C_0$  is equal to the “pure barite” saturation concentration as calculated for the water column (Monnin et al., 1999). In fact, interstitial Ba concentrations are usually higher than the calculated (pure) barite saturation (Church and Wolgemuth, 1972; Gingele and Dahmke, 1994; McManus et al., 1998), indicating that pore waters are probably in equilibrium with a mixed barite–sulfate phase. Accordingly, the benthic Ba fluxes calculated here have probably been underestimated. In addition, it has been demonstrated that shallow sediment receive relatively more labile Ba compared with deep traps (Dymond and Collier, 1996; Dehairs et al., 2000). It was hypothesized that upon settling, barite particles partly recrystallize and become less soluble (McManus et al., 1998). In Figure 11, the calculated benthic Ba fluxes vs. water depth is shown for different values of  $z$ . These theoretical results indicate that the benthic regeneration fluxes at 500 mbss are 10

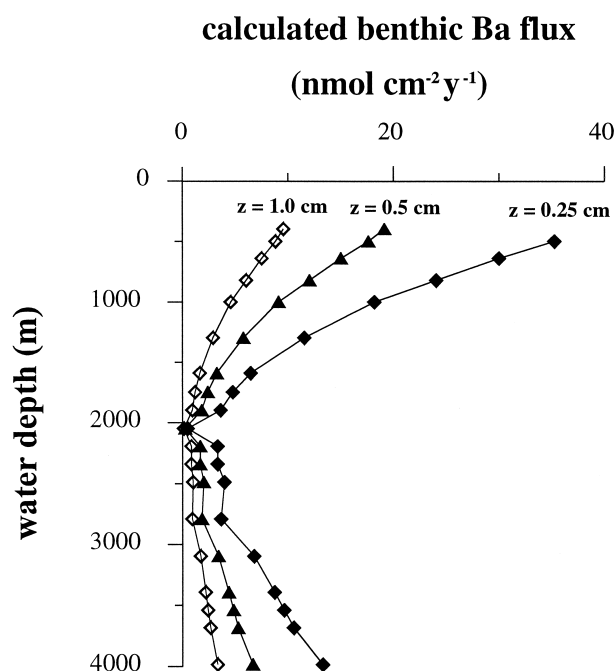


Fig. 11. Plot of theoretical benthic Ba fluxes ( $\text{nmol cm}^{-2} \text{y}^{-1}$ ) vs. water depth for different values of the sediment "saturation" depth  $z$ , calculated with Eqns. 6 and 7 (see text).

times higher as for 2000 mbss. The calculated values are of the same magnitude as Ba fluxes measured by benthic chamber experiments ( $15\text{--}50 \text{ nmol cm}^{-2} \text{y}^{-1}$ ; McManus et al., 1994, 1998) or from pore-water gradients ( $6\text{--}30 \text{ nmol cm}^{-2} \text{y}^{-1}$ ; Paytan and Kastner, 1996). These calculations demonstrate that differences in Ba bottom-water concentration may potentially cause large variations in benthic Ba loss from the sediment and hence in the barite burial efficiency.

It is difficult to determine the main environmental factor controlling Ba preservation in the Arabian Sea because most of the processes influencing sedimentary Ba cycling depend on water depth. However, on the basis of 1) the good correlation between SI and barite accumulation in the upper 2000 m of the water column, 2) the potentially high impact of variations in SI on benthic Ba regeneration, and 3) the conclusion that redox conditions cannot explain the gradual increase in barite preservation with water depth in the upper 2000 m of the water column, we argue that the degree of barite saturation of the bottom water is the most important variable controlling sedimentary Ba preservation. Organic matter degradation, bioturbation, diagenetic Mn cycling, and the crystallinity of the accumulating barite flux may play an additional role. The determination of the relative importance of each of these processes requires further study.

### 3.4. Implications

The application of Ba as a quantitative proxy for export production requires that its preservation upon burial must be quantifiable. As discussed above, Ba preservation is dependent on several environmental conditions, which may have varied through time. First, the barite saturation state of the water

column has not been constant on geologic time scales. This has been documented by the Ba/Ca ratio of benthic foraminifera, which has been used to characterize paleo Ba bottom-water concentrations (Lea and Boyle, 1989). For example, sediment records from the Atlantic Ocean have revealed strong fluctuations in the Ba concentration of the deep waters on a glacial–interglacial time scale, which have been attributed to variations in deep water circulation (Lea and Boyle, 1990; Martin and Lea, 1998). On time periods exceeding the oceanic reservoir age of Ba (ca. 10 kyr; Chan et al., 1977), a higher burial rate of barite may lower the dissolved Ba concentration in the water column and reduce the barite burial efficiency, thus creating a negative feedback. Second, the redox conditions of bottom-water and surface sediment have varied through time. During periods of increased primary productivity, high fluxes of organic matter may promote more oxygen-depleted conditions, affecting bioturbation, Mn cycling, and the rate of sulfate reduction, which in turn will reduce the barite preservation.

Continental margin sediments are generally exposed to bottom waters undersaturated with respect to barite (Monnin et al., 1999), which result in low Ba burial efficiencies. As a consequence, past changes in productivity will leave no, or only a very weakened, Ba signal in these marine environments. Furthermore, the  $\text{Ba}_{\text{det}}/\text{Al}$  of the terrigenous sediment fraction may have varied through time as the result of fluctuations in grain size and provenance of source material. For these regions, therefore, the bulk sedimentary Ba content is not a suitable proxy to quantitatively reconstruct export production, a finding that is in accordance with previous studies (Dymond et al., 1992; Kumar et al., 1996; Fagel et al., 1999; Dehairs et al., 2000). Nevertheless, application of a sequential Ba extraction method allows the detection of small fluctuations in the barite content, which may be used as a qualitative tracer of paleoproductivity.

## 4. CONCLUSIONS

Ba in Arabian Sea surface sediments is incorporated in three major fractions: barite, Ba incorporated in aluminosilicates, and Ba associated with Mn/Fe oxides. Accumulation of barite, which is the most important Ba fraction in sediments located below 2000 mbss, increases gradually with water depth. The Ba/Al ratio of the terrigenous fraction varies significantly across the Arabian Basin as the result of differences in grain size and provenance of the source material. Ba associated with Mn oxides is a relatively minor fraction compared with bulk Ba concentrations and only accumulates in well oxygenated sediments below the present-day OMZ.

The water-depth-dependent accumulation of barite in the Arabian Sea is not related to the continuous formation of barite in settling organic particles or Ba scavenging by Mn oxyhydroxides but is primarily controlled by differences in Ba preservation upon deposition. The good correlation between the barite saturation index and the barite accumulation rate in the upper 2000 m of the water column indicates that the degree of barite saturation of the bottom water is probably the main environmental factor regulating the burial efficiency of barite. Further study should clarify whether the degree of bottom water barite saturation can be used to accurately predict the barite preservation factor. Redox conditions of the bottom

water and sediment may play an additional role. Suboxic organic matter degradation, lack of diagenetic Mn cycling, and low bioturbation rates may have reduced Ba preservation in relative shallow continental margin sediments (500–1000 mbss) underlying the OMZ. No correlation was found between Ba preservation and the mass accumulation rate.

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